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## PATENT OFFICE JAPANESE GOVERNMENT

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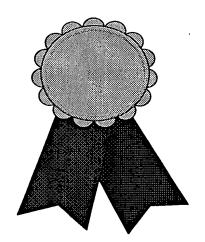
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[Name of Document] SPECIFICATION

[TITLE OF THE INVENTION] IRON-BASE SINTERED ALLOY MATERIAL FOR VALVE SHEET AND PROCESS FOR PREPARING THE SAME

[Claims]

[Claim 1] An iron-base sintered alloy material in which a hard particle is dispersed in a base phase, said iron-base sintered alloy material for a valve sheet characterized in that said hard particle is dispersed at 5 to 40% as an area rate, a porosity is 15 to 25% as a volume rate, and a density after sintering is 6.1 to 6.9 g/cm<sup>3</sup>.

[Claim 2] An iron-base sintered alloy material in which a hard particle is dispersed in a base phase, said iron-base sintered alloy material for a valve sheet characterized in that the composition of a base part containing said base phase and said hard particle has a composition containing a total of 10.0 to 40.0 % selected from 1 or 2 or more selected from Ni: 2.0 to 23.0%, Cr: 0.4 to 15.0%, Mo: 3.2 to 15.0%, Cu: 0.2 to 3.0%, Co: 3.0 to 15.0%, V: 0.1 to 0.5%, Mn: 0.1 to 0.5%, W: 0.2 to 6.0%, C: 0.8 to 2.0%, Si: 0.1 to 1.0% and S: 0.1 to 1.0% expressed as % by mass, and the balance substantially comprising Fe, said hard particle is a particle composed of 1 or 2 or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe, the hard particle is dispersed at 5 to 40% as an area rate, a porosity is 12 to 25% as a volume rate, and a density after sintering is 6.1 to 6.9 g/cm<sup>3</sup>.

[Claim 3] The iron-base sintered alloy material for a valve sheet according to claim 1 or 2, wherein a solid lubricant particle is further dispersed in said base phase at 0.3 to 3.5% as an area rate.

[Claim 4] The iron-base sintered alloy material for a valve sheet according to claim 3, wherein said solid lubricant particle is 1 or 2 or more selected from a sulfide and a fluoride.

[Claim 5] A process for preparing an iron-base sintered alloy material comprising a molding step of filling a raw material powder into a

mold, and compressing and molding the powder to obtain a green compact, and a sintering step of sintering the green compact by heating in the protective atmosphere to obtain a sintered compact, said process for preparing an iron-base sintered alloy material for a valve sheet characterized in that the raw material powder is obtained by incorporating and mixing 20 to 70% of a pure iron powder, 10 to 50% of an alloy iron powder containing a total of 3 to 30% of 1 or 2 or more selected from C, Ni, Cr, Mo, Cu, Co, W, V and Mn, and the balance substantially comprising Fe, and 5 to 40% of a hard particle powder composed of 1 or 2 or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe expressed as % by mass relative to a total amount of a raw material powder, and the compressing and molding conditions in the molding step and the sintering conditions in the sintering step are adjusted so that the sintered compact has a density after sintering of 6.1 to 6.9 g/cm³ and a porosity of 12 to 25% as a volume rate.

[Claim 6] The process for preparing an iron-base sintered alloy material for a valve sheet according to claim 5, wherein a solid lubricant particle powder is further incorporated into the raw material powder at 0.2 to 3.0 parts by weight relative to 100 parts by weight of a total amount of a raw material.

[Claim 7] The process for preparing an iron-base sintered alloy material for a valve sheet according to claim 5 or 6, wherein in place of a part or all of said alloy iron powder, an alloy element powder of 1 or 2 or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C is incorporated at a total amount of 0.3 to 15% as % by weight relative to a total amount of raw material powder.

[Claim 8] A valve sheet made of an iron-base sintered alloy, which comprises, as a material, the iron-base sintered alloy material for a valve sheet according to any one of claims 1 to 4.

[Detailed Description of the Invention]

[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to a sintered alloy material, in particular, an iron-base sintered alloy material which is suitable in a valve sheet for an internal combustion engine.

[0002]

[Prior Art]

A valve sheet plays a roll in sealing a combustion gas and cooling a valve, and has been used by press-fitting into a cylinder-head of an engine. A valve sheet is required to have, in addition to the resistance to heat, the resistance to wear and the resistance to corrosion, the low counterpart aggressiveness so as not to wear a valve which is a counterpart.

[0003]

Recently, in an automobile engine, there is increased demand on improvement in long life, high output, discharge gas cleaning, increase in fuel efficiency and the like. For this reason, a valve sheet for an automobile engine is also required to endure the severer use environment than usual, and it has become necessary to further improve the resistance to heat and the resistance to wear.

In response to such the demand, for example, Patent reference 1 proposes an iron-base sintered alloy material for a valve sheet in which a Cr-Mo-Si-Co series alloy particle as a hard particle is dispersed in a base phase at an area rate of 10 to 30%, and a porosity is 1 to 10% as a volume rate. This iron-base sintered alloy material for a valve sheet is prepared by a process comprising a molding step of filling a raw material powder into a mold, and compressing and molding the powder to obtain a green compact, a primary sintering step of heating and sintering the green compact to a temperature range of 900 to 1200°C in the protective atmosphere to obtain a primary sintered compact, a re-pressing/forging step of re-pressing and forging the primary sintered compact to obtain a re-pressed compact or forged compact having a high density, and a secondary sintering step of sintering the re-

pressed compact or the forged compact at a temperature range of 1000 to 1200°C in the protective atmosphere. According to the technique described in Patent reference 1, a sintered compact having a high density is obtained, and an iron-base sintered alloy material having the improved high temperature strength and thermal conductivity is obtained.

[0004]

In addition, a Patent reference 2 describes a process for preparing a powder metallurgy part, preferable, for valve sheet insert, which comprises compressing and molding a mixture containing 15 to 30% of a valve steel powder, 0 to 10% of Ni, 0 to 5% of Cu, 5 to 15% of a ferroalloy powder, 0 to 15% of a tool steel powder, 0.5 to 5% of a solid lubricant, 0.5 to 2.0% of graphite, 0.3 to 1.0% of a primary lubricant and the balance substantially comprising a low alloy steel powder as expressed as % by mass, and pressing the mixture to an unprocessed density in a range of 6.7 to 7.0 g/cm<sup>3</sup>, preferably to a density of 6.8 to 7.0 g/cm<sup>3</sup>, most preferable 6.9 g/cm<sup>3</sup> to obtain an approximately net-like additive, sintering the additive. According to the technique described in the Patent reference 2, even by one-stage press-sintering method, a relatively high density is obtained, the resistance to wear, the resistance to high temperature, the high creep strength and the high fatigue strength are obtained, and further the resistance to corrosion is improved, and the mechanical processability is improved.

[0005]

[Patent reference 1]

JP-A No. 2000-54087

Patent reference 21

JP-A No. 2000-160307

[0006]

[Problems to be Solved by the Invention]

However, according to the technique described in Patent reference 1, in order to obtain a high density sintered compact having a porosity of 1 to

10%, a re-pressing/forging step and further a secondary sintering step of a sintered compact are necessary and, thus, there is a problem that steps become complicated and the product cost is increased. According to the technique described in Patent reference 2, a relatively high density is obtained by a one-stage molding and one-stage sintering method. However, in order to obtain a high density, a difficult step is required, and, thus, there is a problem that the product cost is increased.

[0007]

Recently, from a viewpoint of the earth environmental conservation, in a gasoline engine (internal combustion engine), improvement in the fuel efficiency is strongly required, a gasoline engine is operated by setting an airfuel ratio (A/F value) at as high as about 12 as compared with an air-fuel ratio (A/F value = about 10) of a mixed gas for the previous internal combustion engine. As a result, there is a problem that a maximum combustion temperature becomes very high due to decreased cooling effect by a gasoline at operation of an internal combustion engine and approaching a theoretical airfuel ratio, and the thermal load applied to a valve sheet is remarkably increased.

[0008]

In addition, when the A/F value of a mixed gas in a gasoline engine becomes high, there is a problem that a combustion gas becomes cleaner than usual, adhesion of the combustion product which is said to have the effect on lubrication of a valve and a valve sheet, and the resistance to wear is lowered.

Further, with a change in such the combustion circumstance in a gasoline engine, iron oxide produced on the surface of a valve and a valve sheet is decreased than usual and, for this reason, there is a problem that adhesive wear is easily caused, and a valve and a valve sheet are remarkably worn.

[0009]

An object of the present invention is to advantageously solve the

aforementioned prior art problems, and provide an iron-base sintered alloy material for a valve sheet which is particularly suitable in recent gasoline engine (internal combustion engine) using a mixed gas having a high A/F value, is excellent in the high temperature strength, the creep strength and the fatigue strength, is excellent in the resistance to wear, and is excellent in the iron oxide producing property, and a process for preparing the same.

[0010]

[Means for Solving the Problems]

In order to attain the above object, the present inventors intensively studied factors influencing on improvement in the resistance to wear of a valve sheet. As a result, the present inventors found that, under the operating environment of the aforementioned recent internal combustion engine, in particular, a gasoline engine (internal combustion engine) in which an A/F value is set high, an amount of iron oxide produced on a sliding surface on a valve sheet by thermal load during operation of an internal combustion engine has the great influence on the resistance to wear of a valve and a valve sheet. Since a highly densified valve sheet has a small porosity, an amount of iron oxide produced on the sliding surface of a valve sheet becomes further small, adhesion wear is easily caused, and wear of a valve and a valve sheet becomes more remarkable. In addition, according to the study of the present inventors, it was found that the mechanical strength dependent on a sintered density has little influence on the resistance to wear.

[0011]

From the foregoing, the present inventors found that, by maintaining the strength, the creep strength, the fatigue strength and the like without increasing a sintered density and, under such the situation, molding a raw material powder into a molded green compact having a relatively low density, sintering the compact to adjust a sintered density relatively low and a porosity in an appropriate range, and making relatively many fine pores present in a sintered compact, production of iron oxide due to thermal load at operation of

an internal combustion engine is promoted, and the compatibility between a valve and valve sheet is improved and, as a result, the resistance to wear is improved.

[0012]

Based on the above findings, we further studied, which resulted in completion of the present invention.

That is, the present invention is an iron-base sintered alloy material in which a hard particle is dispersed in a base phase, said iron-base sintered alloy material for a valve sheet characterized in that the hard particle is dispersed at 5 to 40% as an area rate, a porosity is 12 to 25% as a volume rate, and a density after sintering is 6.1 to 6.9 g/cm<sup>3</sup> and, in the present invention, it is preferable that the composition of a base part containing the base phase and the hard particle has a composition containing a total of 10.0 to 40.0% of 1 or 2 or more selected from Ni: 2.0 to 23.0%, Cr: 0.4 to 15.0%, Mo: 3.2 to 15.0%, Cu: 0.2 to 3.0%, Co: 3.0 to 15.0%, V: 0.1 to 0.5%, Mn: 0.1 to 0.5%, W: 0.2 to 6.0%, C: 0.8 to 2.0%, Si: 0.1 to 1.0% and S: 0.1 to 1.0%, and the balance substantially comprising Fe, and the hard particle is a particle composed of 1 or 2 or more selected from C, Cr, Mo, Co, Si, Ni, S and Fe. In addition, in the present invention, it is preferable that a solid lubricant particle is dispersed in the base phase at 0.2 to 3.5% as an area rate and, in the present invention, it is preferable that the solid lubricant particle is 1 or 2 or more selected from a sulfide and a fluoride.

[0013]

In addition, the present invention is, in a process for preparing an iron-base sintered alloy material comprising a molding step of filling a raw material powder in a mold, and compressing and molding the powder to obtain a green compact, and a sintering step of sintering the green compact by heating in the protective atmosphere to obtain a sintered compact, said process for preparing an iron-base sintered alloy material for a valve sheet characterized in that the raw material powder is obtained by incorporating

and mixing 20 to 70% of a pure iron powder, 10 to 50% of an alloy iron powder containing a total of 3 to 30% of 1 or 2 or more selected from C, Ni, Cr, Mo, Cu, Co, W, V and Mn, and the balance substantially comprising Fe, 5 to 40% of a hard particle powder composed of 1 or 2 or more elements selected from C. Cr. Mo, Co, Si, Ni, S and Fe, as expressed by % by mass relative to a total amount of a pure iron powder, an alloy iron powder and a hard particle powder (total amount of raw material powder), or further 0.2 to 3.0 parts by weight relative to 100 parts by weight of a total amount of a raw material powder of a solid lubricant powder, and the compressing and molding conditions in the molding step and the sintering conditions in the sintering step are adjusted so that the sintered compact has a density after sintering of 6.1 to 6.9 g/cm<sup>3</sup> and a porosity of 12 to 25% as a volume rate and, in the present invention, it is preferable that, in place of a part or all of the alloy iron powder, an alloy element powder of 1 or 2 or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C is incorporated at a total of 0.3 to 15% as % by mass relative to a total amount of a pure iron, an alloy iron powder, an alloy element powder and a hard particle powder (total amount of raw material powder).

[0014]

In addition, the present invention is a valve sheet made of an ironbase sintered alloy prepared using, as a material, any one of the abovementioned iron-base sintered alloy materials for a valve sheet.

[0015]

Embodiment of the Invention

The iron-base sintered alloy material for a valve sheet of the present invention is a sintered compact comprising a base phase, a hard particle dispersed in the base phase, or further a solid lubricant particle dispersed in the base phase, and a pore.

It is preferable that the composition of a base part containing a base phase and a hard particle has a composition containing a total of 10.0 to 40.0% of 1 or 2 or more selected from Ni: 2.0 to 23.0%, Cr: 0.4 to 15.0%, Mo: 3.2 to

15.0%, Cu: 0.2 to 3.0%, Co: 3.0 to 15.0%, V: 0.1 to 0.5%, Mn: 0.1 to 0.5%, W: 0.2 to 6.0%, C: 0.8 to 2.0%, Si: 0.1 to 1.0% and S: 0.1 to 1.0% S expressed by % by mass, and the balance substantially comprising Fe.

[0016]

Ni, Cr, Mo, Cu, Co, V, Mn, W, C, Si and S are all contained in a base phase and a hard particle, are elements for improving the resistance to wear, and can be contained at a total of 10.0 to 40.0% by mass by selecting 1 or 2 or more.

Ni is an element for improving the hardness and the resistance to heat in addition to resistance to wear. When Ni is contained at an amount smaller than 2.0% by mass, the above-mentioned effect is not recognized. On the other hand, when Ni is contained at an amount larger than 23.0% by mass, the counterpart aggressiveness is increased. Preferably, Ni is contained at an amount larger than 5.0% by mass.

[0017]

Cr is contained in a base phase and a hard particle, and is an element for improving the hardness and the resistance to heat in addition to the resistance to wear. When Cr is contained at an amount smaller than 0.4% by mass, the above-mentioned effect is not recognized. On the other hand, when Cr is contained at an amount larger than 15.0% by mass, the counterpart aggressiveness is increased. The amount of Cr is preferable on a range of from 3.0 to 10.0% by mass.

Mo is contained in a base phase and a hard particle, and is an element for improving the hardness and resistance to heat in addition to the resistance to wear. When Mo is contained at an amount smaller than 3.2% by mass, the above mentioned effect is not recognized. On the other hand, when Mo is contained at an amount larger than 15.0% by mass, the counterpart aggressiveness is increased.

[0018]

Cu is an element for reinforcing a base phase and for increasing the

hardness in addition to the resistance to wear. When Cu is contained at an amount smaller than 0.2% by mass, the above-mentioned effect is not recognized. On the other hand, when Cu is contained at an amount larger than 3.0% by mass, the counterpart aggressiveness is increased.

Co is an element having the action of reinforcing binding between a hard particle and a base phase in addition to improvement in the resistance to wear, and having the action of improving the resistance to heat. When Co is contained at an amount smaller than 3.0% by mass, the above-mentioned effect is not recognized. On the other hand, when Co is contained at an amount larger than 15.0% by mass, the counterpart aggressiveness is increased.

[0019]

V is an element for reinforcing a base phase, and for increasing the hardness in addition to the resistance to wear. When V is contained at an amount smaller than 0.1% by mass, the above-mentioned effect is not recognized. On the other hand, when V is contained at an amount larger than 0.5% by mass, the counterpart aggressiveness is increased.

Mn is an element for reinforcing a base phase, and for increasing the hardness in addition to the resistance to wear. When Mn is contained at an amount smaller than 0.1% by mass, the above-mentioned effect is not recognized. On the other hand, when Mn is contained at an amount larger than 0.5% by mass, the counterpart aggressiveness is increased.

[0020]

W is an element for reinforcing a base phase, and for increasing the hardness in addition to the resistance to wear. When W is contained at an amount smaller than 0.2% by mass, the above-mentioned effect is not recognized. On the other hand, when W is contained at an amount larger than 6.0% by mass, the counterpart aggressiveness is increased.

C is an element for improving the base phase reinforcing and sintering diffusibility in addition to the resistance to wear. When C is contained at an

amount smaller than 0.8% by mass, the above-mentioned effect is not recognized. On the other hand, when C is contained at an amount larger than 2.0% by mass, the counterpart aggressiveness is increased.

[0021]

Si and S are elements for improving the strength of a base phase in addition to the resistance to wear. When Si is contained at an amount smaller than 0.1% by mass, and S is contained at an amount smaller than 0.1% by mass, respectively, the above-mentioned effect is not recognized. On the other hand, when Si is contained at an amount larger than 1.0% by mass, and S is contained at an amount larger than 1.0% by mass, the counterpart aggressiveness is increased.

In addition, when a total content of the aforementioned components is less than 10.0% by mass, the hardness of the base phase, and the high temperature properties such as the high temperature strength and the creep strength are reduced. On the other hand, when the total content exceeds 40.0% by mass, the counterpart aggressiveness is increased. For this reason, in the present invention, it is preferable that the total content of the aforementioned components is limited to a range of 10.0 to 40.0% by mass.

[0022]

In a base part, the balance other than the above-mentioned components is substantially Fe.

In addition, a hard particle dispersed in a base phase makes a contribution to improvement in the resistance to wear. In the present invention, its dispersion amount is 5.0 to 40.0% as an area rate. When a hard particle is dispersed at an amount less than 5.0% as an area rate, the abovementioned effect can not be expected. On the other hand, when the particle is dispersed at an amount larger than 40.0%, the counterpart aggressiveness is increased. For this reason, in the present invention, a hard particle is limited to 5.0 to 40.0% as an area rate. Preferably, an area rate is 10.0 to 30.0%.

#### [0023]

It is preferable that a hard particle to be dispersed in the base phase is a particle comprising 1 or 2 or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe. It is preferable that a hard particle has the aforementioned composition and, further, has the hardness in a range of Hv 600 to 1200. When the hardness of a hard particle is less than Hv 600, the resistance to wear is reduced. On the other hand, when the hardness exceeds Hv1200, the toughness is reduced, and a risk of occurrence of chipping and crack is increased.

#### [0024]

Examples of such the hard particle include a Cr-Mo-Co series intermetallic compound particle, a Ni-Cr-Mo-Co series intermetallic compound particle, a Fe-Mo alloy particle, a Fe-Ni-Mo-S series alloy particle and a Fe-Mo-Si alloy particle.

The Cr-Mo-Co series intermetallic compound particle is an intermetallic compound containing 5.0 to 20.0% of Cr and 10.0 to 30.0% of Mo expressed as % by mass, and the balance substantially comprising Co. The Ni-Cr-Mo-Co series intermetallic compound particle is an intermetallic compound comprising 5.0 to 20.0% of Ni, 15.0 to 30.0% of Cr, 17.0 to 35.0% of Mo expressed as % by mass, and the balance substantially containing Co. The Fe-Mo alloy particle is an alloy particle comprising 50.0 to 70.0% of Mo and the balance substantially containing Fe expressed as % by mass. The Fe-Ni-Mo-S series alloy particle is an alloy particle comprising 50.0 to 70.0% of Ni, 20.0 to 40.0% of Mo, 1.0 to 5.0% of S, and the balance substantially containing Fe expressed by % by mass. The Fe-Mo-Si alloy particle is an alloy particle comprising 5.0 to 20.0% of Si, 20.0 to 40.0% of Mo, and the balance substantially containing Fe expressed by % by mass.

#### [0025]

In addition, in the present invention, a solid lubricant particle may be dispersed in a base phase in addition to the hard particle. The solid lubricant

particle has the effect of improving the machinability and the resistance to wear, and decreasing the counterpart aggressiveness. As the solid lubricant particle, 1 or 2 or more selected from sulfides such as MnS and MoS<sub>2</sub> and fluorides such as CaF<sub>2</sub>, and a mixture thereof are preferable. It is preferable that the solid lubricant particle is dispersed at a total of 0.3 to 3.5% as an area rate. When an amount of solid lubricant particle is less than 0.3%, the amount of the solid lubricant particle is small, the machinability is deteriorated, occurrence of adhesion is promoted, and the resistance to wear is reduced. On the other hand, even when the solid lubricant particle is dispersed at an amount larger than 3.5%, the effect becomes saturated, the effect corresponding to the content can not be expected. For this reason, it is preferable that an area rate of the solid lubricant particle is limited to 0.3 to 3.5%.

#### [0026]

In addition, the iron-base sintered alloy material for a valve sheet of the present invention contains a porosity of 12 to 25% expressed by a volume rate. The presence of a pour influences on the high temperature strength, a fatigue strength and the thermal conductivity. When a porosity is less than 12%, production of iron oxide effective for the resistance to wear becomes insufficient at operation of an internal combustion engine using a mixed gas having a high A/F value. On the other hand, when a porosity exceeds 25%, reduction of the strength such as the normal temperature strength, the high temperature strength and the like becomes remarkable. For this reason, in the present invention, a porosity is limited to 12 to 25% as a volume rate. As a porosity referred in the present invention, a value measured by an image analyzing method is used.

#### [0027]

In addition, the iron-base sintered alloy material for a valve sheet of the present invention has a density after sintering of 6.1 to 6.9 g/cm<sup>3</sup>. The density after sintering influences on the high temperature strength, the fatigue strength, and the thermal conductivity. When the density after sintering is less than 6.1 g/cm³, reduction of these strength and thermal conductivity is remarkable. On the other hand, when the density exceeds 6.9 g/cm³, in particular, when an internal combustion engine using a mixed gas having a high A/F value is operated, production of iron oxide effective for the resistance to wear becomes insufficient and, moreover, steps become complicated due to increase in a density, leading to a sudden rise of the manufacturing cost. For this reason, in the present invention, the density after sintering is limited to a range of 6.1 to 6.9 g/cm³.

[0028]

It is preferable that the tissue of a base phase is a tissue composed of 30 to 60% of a pealite phase and 40 to 70% of a high alloy diffusion phase, as an area rate, letting an area of a base phase except for the hard particle to be 100%.

In order to obtain the iron-base sintered alloy material of the present invention, first, to be the composition of base part containing the base phase and the hard particle, 20 to 70% of a pure iron powder, 10 to 50% of an alloy iron powder containing a total of 3 to 30% of 1 or 2 or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C, and the balance substantially comprising Fe, and 5 to 40% of a hard particle powder composed of 1 or 2 or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe expressed as % by mass relative to a total amount of a raw material powder (a total amount of pure iron powder, alloy iron powder, and hard particle powder) as a material powder are blended, or further 0.2 to 3.0 parts by weight of a solid lubricant powder is incorporated relative to 100 parts by weight of a total amount of a raw material powder (pure iron powder, alloy iron powder, and a hard particle powder), and the materials are kneaded to obtain a mixed powder. In addition, as a lubricant, zinc stearate or the like may be further incorporated.

[0029]

When a blending amount of a pure iron powder to be blended as a raw

material powder is less than 20% by mass, an amount of production of iron oxide effective for improvement in the resistance to wear is deficient, and the resistance to wear is reduced. On the other hand, when the amount exceeds 70% by mass, an amount of produced iron oxide becomes larger, but the hardness of a base phase is reduced, and the resistance to wear is reduced at an operation initial stage before production of iron oxide.

An alloy iron powder is incorporated in order to increase the hardness of a base phase and the high temperature strength. When an amount of an alloy iron powder to be incorporated is less than 10%, the aforementioned effect is deficient. On the other hand, when the amount exceeds 50%, the above mentioned effect becomes saturated, and the effect corresponding to an incorporation amount can not be expected, being disadvantageous. An alloy iron powder contains a total of 3 to 30% by weight of 1 or 2 or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C, and the balance substantially comprising Fe. When the content of 1 or 2 or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C in an alloy iron powder is less than a total of 3% by mass, the effect of incorporation of the aforementioned alloy iron powder is not perceived. On the other hand, when the above-mentioned alloy elements are contained in an alloy iron powder at a total amount larger than 30% by mass, the aforementioned effect becomes saturated, and the effect corresponding to an incorporation amount can not be expected, being economically disadvantageous.

[0030]

A hard particle powder composed of 1 or 2 or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe is incorporated from a viewpoint of improvement in the resistance to wear. When an incorporation amount thereof is less than 5% expressed as % by mass relative to a total amount of a raw material powder, the aforementioned effect can not be expected. On the other hand, when the powder is incorporated at an amount larger than 40%, the counterpart aggressiveness is increased.

In addition, a solid lubricant particle powder is incorporated as necessary in order to improve the machinability and the resistance to wear, and decrease the counterpart aggressiveness. When an incorporation amount is less than 0.2 parts by mass relative to 100 parts by mass of a total amount of a raw material (total amount of pure iron powder, alloy iron powder and a hard particle powder), the machinability is deteriorated, and the resistance to wear is reduced. On the other hand, when the powder is incorporated at an amount larger than 3.0 parts by mass, the effect becomes saturated, and the effect corresponding to the content can not be expected.

[0031]

In addition, in the present invention, it is preferable that, in place of a part or all of the aforementioned alloy iron powder, an alloy element powder of 1 or 2 or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C is incorporated at 0.3 to 15% expressed as % by mass relative to a total amount of a raw material powder (a total amount of pure iron powder, alloy iron powder, alloy element powder, and hard particle powder). Ni, Cr, Mo, Cu, Co, V, Mn, W and C powders can be all incorporated by selection in place of an alloy iron powder, in order to potentiate the hardness of a base phase and the high temperature strength. When a total incorporation amount of these alloy element powders is less than 0.3 % by mass, the hardness of a base phase and the high temperature strength are low, and the resistance to wear is reduced. On the other hand, even when those powders are incorporated at an amount larger than 15% by mass, the effect becomes saturated, and the effect corresponding to the content can not be expected.

[0032]

It is preferable that the aforementioned pure iron powder, alloy iron powder and alloy element powder, hard particle powder, or further solid lubricant powder are incorporated at a predetermined amount, and mixed and kneaded to obtain a mixed powder.

In the present invention, an iron-base sintered alloy material for a

valve sheet is obtained via a molding step of filling the mixed powder into a mold, and compressing and molding the powder with a molding press or the like to obtain a green compact, and a sintering step of sintering by heating the green compact to a temperature range of, preferably, 1000 to 1200°C in the protective atmosphere such as ammonia degrading gas and the like.

[0033]

In the present invention, it is preferable to adjust the press molding conditions in a molding step and the sintering conditions in a sintering step so that a density after sintering of a sintered compact becomes 6.1 to 6.9 g/cm<sup>3</sup> and a porosity becomes 12 to 25% expressed as a volume rate. It is preferable from a viewpoint of control of a density after sintering that, in a molding step, so that a density of a green compact becomes 6.2 to 7.0 g/cm<sup>3</sup>.

The resulting sintered compact (iron-base sintered alloy material) is subjected to cutting and grinding processes to obtain a valve sheet having desired size and shape.

[0034]

[Examples]

As a raw material powder, kinds shown in Table 1 of an alloy iron powder or alloy element powder, a hard particle powder, or further a solid lubricant powder were incorporated into pure iron powder at amounts shown in Table 1, and the materials were mixed and kneaded to obtain a mixed powder. An incorporation amount of each raw material powder is expressed as % by mass relative to a total amount of (pure iron powder + alloy iron powder or alloy element powder + hard particle powder). An amount of a solid lubricant powder to be incorporated is expressed as parts by weight relative to 100 parts by weight of a total amount of a raw material powder (pure iron powder + alloy iron powder or alloy element powder + hard particle powder).

[0035]

Then, the mixed powder was filled into a mold, and compressed and

molded by a molding press to obtain a green compact. The conditions of compressing and molding were changed to adjust a density of a green compact.

Then, the green compact was subjected to a sintering step of sintering for 10 to 30 minutes in the protected atmosphere (ammonia degrading gas) at 1000°C to 1200°C and was obtained a sintered compact (iron-base sintered alloy material).

[0036]

A test sample was collected from the resulting sintered compact, and the composition of a base part, a porosity of a sintered compact, and a density after sintering were measured. A porosity was measured by an image analyzing method. A density was obtained by an Archimedes method.

From the resulting sintered compact, a valve sheet (size and shape:  $\phi$  33mm  $\times \phi$  29mm  $\times$  6.0mm) was processed by a cutting process and a grinding process, and a simple rig wear test (resistance to wear confirming test) and an oxidation test (iron oxide production amount confirming test) were performed.

[0037]

(1) Simple rig wear test (resistance to wear confirming test)

A simple rig test was performed using a simple rig wear test machine shown in Fig. 4. After a valve sheet 1 was press-fitted into a tool 2 corresponding to a cylinder head, a valve 4 was moved up and down by the crank mechanism while heating a valve 4 and a valve sheet 1 by a heat source (LPG + Air) 3 mounted on a test machine, and a wear amount was measured as a valve sinking amount. The test conditions are as follows:

[0038]

Test temperature: 400°C (sheet surface)

Test time: 9.0 hr

Cam rotation: 3000 rpm

Valve rotation: 20 rpm

Spring role: 35 kgf (345N) (at setting)

Valve material: SUH35

Lift amount: 9.0 mm

(2) Oxidation test (iron oxide production amount confirming test)

After a valve sheet was defatting-washed, it was placed into a heating furnace, thermal treatment was performed under the following test conditions:

Heating temperature: 300, 400, 500°C

Heating time: 2h

Heating atmosphere: atmospheric atmosphere,

weights before and after thermal treatment were measured, and an amount increased by oxidation was obtained. An amount increased by oxidation (%) was calculated by [ {(weight after thermal treatment) - (weight before thermal treatment) }/(weight before thermal treatment) ]  $\times$  100 (%).

[0039]

The resultant results are shown in Table 2.

[0040]

[Table 1]

			Raw mate	Solid	lubricant powder	Green compact					
Test No.				Alloy element powde	Total of incorporation amount	Hard p	Incorporation	Kind <sup>™</sup>	Incorporation amount (parts by weight relative to 100 parts by weight of raw material powder)	Density g/cm³	
1	40.0	С	45.0	C:1.0	1.0	d	14.0	(B)	1.0	6.70	
2	42.9	В	45.0	C:1.1	1.1	а	11.0	(A)	0.5	6.70	
3	68.8	-	-	C:1.2, Ni:5.0, Co:5.0	11.2	b	20.0	(A)	0.5	6.60	
4	63.8	-	-	C:1.2, Ni:6.0, Co:4.0, Mo:3.0	14.2	b	22.0	(B)	1.0	6.55	
5	40.9	Α	40.0	C:1.1	1.1	С	18.0	(A)	2.0	6.55	
6	65.8	-	•	C:1.2, Ni:6.0, Co:4.0, Cu:3.0	14.2	С	20.0	(B)	2.0	6.45	
7	22.0	D	45.0	C:1.0	1.0	d	32.0	(B)	1.0	6.50	
8	64.8	Ε	14.0	C:1.2	1.2	d	d 20.0		1.0	6.45	
9	65.0	F	12.0	C:1.0	1.0	а	22.0	(A)	0.5	6.40	
10	38.7	В	40.0	C:1.3	1.3	а	20.0	(A)	1.5	6.20	
11	64.8	-	-	C:1.2, Ni:6.0, Co:3.0	10.2	b	b 25.0		1.0	6.15	
12	60.7	-	-	C:1.3, Ni:6.0, Co:4.0, Cu:3.0	14.3	с 25.0		(B)	1.0	6.15	
13	39.8	С	45.0	C:1.2	1.2	d	14.0	(B)	1.0	7.05	
14	38.0	E	40.0	C:2.0	2.0	а	20.0	(A)	1.5	6.10	
15	14.7	F	60.0	C:1.3	1.3	ď	24.0	(B)	0.5	6.50	
16	90.1	Α	5.0	C:0.9	0.9	b	4.0	-	-	6.50	
17	17.4	В	31.5	C:1.1	1.1	d	50.0	(B)	2.5	6.20	
18	83.7	-		C:1.1, Ni:0.2	1.3	b	15.0	(A)	0.3	6.00	
19	40.0	С	45.0	C:1.0	1.0	ď	14.0	(B)	1.0	6.85	
20	40.0	С	45.0	C:1.0	1.0	d	14.0	(B)	1.0	7.00	
21	61.0	C	20.0	C:1.0	1.0	b	18.0	(A)	0.5	6.86	
22	68.8	E	10.0	C:1.2	1.2	d	20.0	(B)	1.0	6.75	

\*) Alloy iron powder;

A: 1.0Cr-0.5Mn-0.3-Mo-bal.Fe
B: 3.0Cr-0.2Mo-bal.Fe
C: 4.0Ni-1.5Cu-0.5Mo-bal.Fe
D: 1.5C-12Cr-1Mo-1V-bal.Fe (SKD11)
E: 0.8C-4Cr-5Mo-2V-6W-bal.Fe (SKH51)
F: 1.2C-4Cr-3Mo-10W-3V-10Co-bal.Fe (SKH57)
e powder;
(A): MnS
(B): CaF<sub>2</sub>

\*\*\*) Solid lubricant particle powder;

\*\*) Hard particle powder; a: Cr-Mo-Co series intermetallic compound (Hv: 700) b: Ni-Cr-Mo-Co series intermetallic compound (Hv: 1100) c: Fe-Mo series hard particle (Hv: 1100) d: Fe-Ni-Mo-S series hard particle (Hv: 600)

[0041]

[Table 2]

		Note		Example of present invention	Comparative Example	Comparative Example	Comparative Example	Comparative Example	Comparative Example	Comparative Example	Example of present invention														
Test result		oxidation	200°C	0.74	0.76	0.81	0.87	0.73	0.84	0.67	0.81	0.83	0.87	0.97	0.97	0.13	96.0	0.14	0.88	0.87	0.93	0.79	0.82	0.76	0.75
	Oxidation test	Amount increased by oxidation (%)	400°C	0.58	0.58	09:0	0.65	0.52	0.64	0.52	0.61	0.64	0.62	0.71	0.73	0.05	0.73	0.07	99.0	0.72	0.73	0.63	0.65	0.65	0.62
	O	Amount in	300°C	0.21	0.26	0:30	0.32	0.24	0:30	0.18	0.27	0:30	0.28	0.33	0.29	0.01	0.25	0.02	0.21	0.20	0.29	0.25	0.28	0.23	0.25
	П	unt (µm)	Valve	7	80	#	10	7	10	13	6	10	6	80	10	25	56	38	25	58	28	10	4	12	6
	Simple rig test	Wear amount (µm)	Sheet	14	16	14	12	13	11	10	17	13	12	10	11	35	52	44	26	28	54	12	16	15	17
	Penery	Density after sintering g/cm³		6.60	6.58	6.55	6.48	6.45	6.40	6.45	6.40	6.35	6.15	6.12	6.10	7.01	6.02	6.47	6.45	6.15	0.00	6.75	6.90	6.75	6.80
		Porosity Volume %		16.5	17.0	17.0	19.0	20.0	20.5	20.2	20.5	21.5	23.5	24.0	24.0	10.0	30.5	20.0	20.5	24.0	25.5	15.0	12.0	14.0	16.0
	File	Solid lubricant particle Area %		1.2	0.7	0.7	1.2	2.3	2.3	1.2	1.2	0.7	1.7	1.2	1.2	1.2	1.7	0.7		3.0	0.5	1.2	1.2	0.7	1.2
		Hard particle Area %		12.0	10.0	18.0	20.0	16.0	18.0	30.0	18.0	20.0	18.0	23.0	23.0	12.0	18.0	22.0	3.0	45.0	13.0	12.0	12.0	16.0	18.0
		Balance		Fe	Fe	Fe	Fe	Fe	e e	Fe	Fe	Fe	Fe	Fe											
Sintered compact		ð	alloy element	17.2	13.6	31.2	36.2	11.9	26.2	39.1	23.2	26.7	22.6	35.2	29.3	17.6	29.2	43.2	5.0	51.1	16.3	17.4	17.4	20.7	22.5
	by ma	Signal Co		Si:0.1, S:0.4	V:0.1, Si:0.3	Si:0.4	Si:0.4	Mn:0.3	•	V:0.4, Si:0.2, S:0.9	V:0.3, W:0.8, Si:0.2, S:0.5	V:0.4, W:1.1, Si:0.6	V:0.1, Si:0.5	Si:0.5	•	Si0.1, S:0.4	V:0.8, Mn:0.1, W:2.3, Si:0.6	V.2.0, Si:0.3, S:0.6, W:5.5	Si:0.1	V:0.1, Si:0.4, S:1.4	Si:0.3	Si:0.1, S:0.4	Si:0.1, S:0.4	Mn:0.3, Si:0.4, S:0.2	V:0.2, W:0.6, Si:0.2, S:0.5
	Base part composition (%	8		•	6.6	13.0	12.8	٠	4.0	•	٠	14.3	12.0	13.0	4.0	•	12.0	5.6	1.6		0.9	•	•	7.2	,
	Base po	- d		0.7	•	-	•	•	3.0	• ,	-	-		-	3.0	0.7	•		,	,	•	0.7	0.7	0.3	•
		. 8		4.0	3.2	4.8	8.3	10.1	12.0	9.4	6.3	6.7	5.8	6.0	15.0	4.2	7.7	8.9	1.0	14.1	3.6	4.2	4.2	4.4	6.1
		Ö	i	,	2.3	4.8	5.3	0.4	,	5.4	9.0	2.4	2.9	6.0		,	3.3	2.5	1.0	1.0	3.6		•	4.3	0.4
		ž		11.0		7.0	8.2	٠	0.9	21.1	13.2	•	•	8.5	0.9	11.0	•	15.8	0.4	33.0	1.7	11.0	11.0	2.6	13.2
Ц		O		1.0	1.1	1.2	1.2	7:	1.2	1.7	1.3	1.15	1.3	1.2	1.3	1.2	2.4	2.0	6.0	<del>1</del> -	1.	<u>5</u>	1.0	1.0	1.3
L	No.			-	5	က	4	သ	ဖ	7	80	ი	10	Ξ	12	13	14	15	16	17	18	6	20	21	22

[0042]

In Examples of the present invention (test No. 1 to No. 12, No. 19 to No. 22), wear amounts of a valve sheet are 10 to 17 μm, wear amounts of counterparts are 7 to 13 µm, an amount increased by oxidation in each test temperature is large, and an iron-base sintered alloy material satisfying the excellent resistance to wear and the excellent iron oxide production property at the same time is obtained. On the other hand, in Comparative Examples outside the scope of the present invention (test No. 13 to No. 18), wear amounts of a valve sheet are 28 to 54 µm, and wear amounts of a counterpart are 25 to 58 µm and, as compared with Example of the present invention, the resistance to wear is reduced, the counterpart aggressiveness is increased, and an amount increased by oxidation is constant and is not increased and, thus, the excellent resistance to wear and the excellent iron oxide production property are not satisfied at the same time. In particular, in a test No. 13 (Comparative Example) having a great density after sintering, a valve and a valve sheet have greater wear amounts than those of Examples of the present invention. In a test No. 14 (Comparative Example) having a great porosity and a small density after sintering, in particular, a wear amount of a valve sheet is great.

[0043]

One example of the texture of the resulting iron-base sintered alloy material is shown in Fig. 1, Fig. 2 and Fig. 3.

Fig. 1 (a) shows the light microscope texture of a base part in a test No. 2 (Example of present invention), and (b) is a sketch view of (b). A base part has a hard particle (H) and a solid lubricant part dispersed in a base phase. The texture of a base phase is composed of perlite (P) and high alloy diffusion phase (R). V is a pore.

[0044]

Fig. 2 (a) is the light microscope tissue of a base part in a test No. 5 (Example of present invention), and (b) is a sketch view of (a).

Fig. 3 (a) is the light microscope tissue of a base part in a test No. 14 (Comparative Example), and (b) is a sketch view of (b).

[0045]

[Effects of the Invention]

According to the present invention, an iron-base sintered alloy material excellent in the resistant to wear and the iron oxide production property is obtained, and this material as an automobile valve sheet shows the excellent durability to severe operation of a engine having a high A/F value, exerting the especial industrial effect.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 (a) is a photograph showing the light microscopic texture of an iron-base sintered alloy material of Example (test No. 3) of the present invention, and Fig. 1 (b) is a sketch view of (a).

[Fig. 2]

Fig. 2 (a) is a photograph showing the light microscopic texture of an iron-base sintered alloy material of Example (test No. 5) of the present invention, and Fig. 2 (b) is a sketch view of (a).

[Fig. 3]

Fig. 3 (a) is a photograph showing the light microscopic texture of an iron-base sintered alloy material of Comparative Example (test No. 14), and Fig. 3 (b) is a sketch view of (a).

[Fig. 4]

Fig. 4 is a schematic view for explaining a simple rig wear tester.

[Explanation of the Numerals]

- 1 Valve sheet
- 2 Tool
- 3 Heat source
- 4 Valve
- P Perlite

- H Hard particle
- R High alloy diffusion phase
- V Pore

[Name of Document] ABSTRACT

[Abstract]

[Object] Is to provide an iron-base sintered alloy material for a valve sheet excellent in the resistance to wear and a process for preparing the same. [Solving Means] An iron-base sintered alloy material for a valve sheet is a material in which a hard particle composed of 1 or 2 or more elements selected from C, Cr, Mo, Co, Si, Ni, S and Fe is dispersed in a base phase, a porosity is 15 to 25% as a volume rate, and a density after sintering is 6.1 to  $6.9 \text{ g/cm}^3$ . Thereby, production of iron oxide at operation of an internal combustion engine is promoted, and the resistance to wear is remarkably improved. It is preferable that a base part containing a base phase and the hard particle has the composition containing a total of 10.0 to 40.0% of 1 or 2 or more selected from Ni, Cr, Mo, Cu, Co, V, Mn, W and C, and the balance substantially comprising Fe. It is preferable that a solid lubricant particle of 1 or 2 or more selected from a sulfide and a fluoride is further dispersed in a base phase at 0.3 to 3.5% as an area rate.

[Selected Drawing] Figure 1